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(54) METHOD OF ENGRAVING WITH IMAGE MASK AND PHOTSENSITIVE LAMINATE FILM FOR SAID IMAGE MASK

GRAVIERVERFAHREN MIT BILDMASKE UND LICHTEMPFLINDLICHER LAMINATFILM FÜR
BESAGTE BILDMASKE

PROCEDE DE GRAVURE AVEC MASQUE A IMAGE, ET FILM STRATIFIE PHOTSENSIBLE
POUR LEDIT MASQUE

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(56) References cited:
JP-A- 58 196 971 JP-A- 60 104 938
JP-A- 60 104 939 US-A- 4 430 416
US-A- 4 764 449

• PATENT ABSTRACTS OF JAPAN vol. 010, no.
364 (P-524) 5 December 1986 & JP-A-61 160 748
(ASAHI CHEM IND CO LTD) 21 July 1986
• PATENT ABSTRACTS OF JAPAN vol. 007, no.
286 (P-244) 21 December 1983 & JP-A-58 159 530
(NIPPON GOSEI KAGAKU KOGYO KK) 21
September 1983

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Description

Technical Field

[0001] The present invention relates to a method for forming images by engraving through sand blasting or by etching with chemicals, for instance, solutions of etching agents through an image-carrying mask such as picture images, patterns or letters on the surface of materials to be processed such as glass, stone, pottery, metals, plastics, wooden materials and leather as well as a photo-sensitive laminate film for use in making such an image-carrying mask.

Background Art

[0002] Conventionally known methods for processing the surface of a material such as glass, a metal or a plastic by engraving images on the surface comprise the steps of first forming a resist layer, in the form of images, on the surface of a material to be processed and then subjecting the entire surface inclusive of the surface of the resist layer to sand blasting to thus engrave the surface on which any image is not present and to thereby form the images thereon. When the material to be processed is glass, a treatment of the surface with hydrofluoric acid can be substituted for the sand blasting treatment and thus desired images can be formed on the surface through engraving and/or etching of the surface portion on which any image is not present. On the other hand, when the material to be processed is a copper plate, the surface can also be treated with an aqueous solution of ferric chloride and thus the desired images can be formed through engraving and/or etching of the surface portion on which any image is not present.

[0003] The formation of a resist layer can be performed according to a method which comprises printing desired images on the surface of a material to be processed with a resist ink according to the screen printing method to thus form a resist layer in the form of desired images. Alternatively, a resist layer can also be formed by likewise printing images on the surface of a non-woven fabric of glass fibers according to the screen printing method and then adhering the resulting non-woven fabric carrying the printed images to the surface of a material to be processed.

[0004] Moreover, there have been proposed a variety of methods for preparing image-carrying masks using liquid photo-sensitive resins. For instance, Japanese Patent Publication for Opposition Purpose (hereunder referred to as "J.P. KOKOKU") No. Sho 46-35681 discloses a method for producing an image carrying mask which comprises the steps of enclosing a predetermined surface area of a material to be processed such as glass with a rubber frame, directly pouring a photo-sensitive resin into the enclosed area, covering the area with a cellophane film, exposing the resin to

light through a negative film carrying pictures and/or patterns, peeling off the cellophane film and then developing the imagewise exposed photo-sensitive resin to thus form a resist layer carrying the desired images.

[0005] Japanese Patent Unexamined publication (hereunder referred to as "J.P. KOKAI") No. Sho 53-99258 discloses a method for producing an image-carrying mask which comprises sandwiching a liquid photo-sensitive resin composition between two transparent films to form a photo-sensitive resin composition between two transparent films to form a photo-sensitive layer, exposing the liquid photo-sensitive resin layer to light while coming the composition in close contact with a photomask carrying desired pictures and/or patterns, peeling off the transparent film on the side of the photomask, removing the unexposed areas of the layer to thus give the desired image, adhering the resulting photo-sensitive resin layer on which the images are thus formed to the surface of a material to be processed so that the face of the former on the photomask side opposes to the surface of the material and peeling off the remaining transparent film.

[0006] J.P. KOKAI No. Sho 55-96270 discloses a method which comprises the steps of putting a molding frame which also serves as a spacer on a support layer (for instance, a polyester film having a thickness of 100 μ m) capable of being treated by sand-blasting, pouring a liquid photo-sensitive resin (100% modulus of the resin photo-hardened = 500 kg/cm²) into the area defined by the molding frame, exposing the resin to light through a film carrying pictures and/or patterns, developing the exposed resin to thus give a mask carrying the images which comprises photo-hardened photo-sensitive resin layer having through holes corresponding to the images, applying a rubber paste to the reverse face of the support and then adhering the resulting product to the surface of a material to be processed. In addition, J.P. KOKAI No. Sho 60-104939 discloses a transfer material for forming a mask for sand blasting which comprises a layer carrying a mask-pattern formed from a liquid photosensitive resin composition in which the molecular structure and the properties of its components are specified; a substrate layer for supporting the layer carrying the mask-pattern; and a support layer which is placed between the layer carrying the mask-pattern and the substrate layer, which can be well-adhered to the layer carrying the mask-pattern but is capable of being peeled off from the substrate layer and which can be destroyed through sand blasting. In the washing away development of these photo-sensitive resin compositions, it is needed to use an organic solvent such as acetone or benzene; an alkaline aqueous solution such as an aqueous sodium hydroxide or sodium borate solution; an alcoholic solution of calcium chloride or an aqueous solution of a surfactant such as a neutral detergent as a developer.

[0007] US-A-4 764 449 relates to a resist laminate for adherent application to the surface of an object

which is to be partially etched. A water-soluble polymer and a photo-crosslinking agent for such a polymer, thus providing photo-crosslinkability, is used in the form of a photo-sensitive laminate film for the etching method. The method for etching a material according to this document is practiced by means of two embodiments. In one embodiment, a complete unit comprising an object to be processed, an adhesive layer, a support membrane and a resist layer (which is partially photo-crosslinked) is subjected to a water-dissolution step for removing the non-crosslinked portion of the resist layer. The method then comprises a subsequent sand-blasting step for removing the support membrane and the adhesive layer under the dissolved portion, and finally an etching step for removing the remainder of the photo-crosslinked resist layer, membrane support and adhesive layer. In the other embodiment, after the photo-crosslinked resist layer portion is formed on the support membrane, the resulting laminate film is adhered to the substrate to be processed by providing an adhesive layer between the resist layer and the substrate.

[0008] The present invention has been completed under such circumstances and the object of the present invention is to provide a method for engraving or etching images with a mask carrying such images as well as a photo-sensitive laminate film for use in making a mask carrying images, which makes it possible to easily and precisely form fine precise images on a mask according to the photoprinting technique in the production of such a mask which is used when images are engraved or etched on the surface of a material to be processed such as glass, a metal or a plastic; which can be handled in the form of a film; which can easily be exposed to light and developed; which can be developed with a developer simply comprising water and whose handling is thus safe and economical; whose surface carrying images obtained after development has strong adhesion and thus can be adhered to the surface of a material to be processed without using any adhesive to thus transfer images to the material; whose substrate can easily be peeled off after fine pictures and/or patterns are transferred to the material to thus prevent the aberration of the position of an image; and which makes it possible to prevent the removal of fine portions of images during sand blasting to thus allow precise engraving and/or etching.

Disclosure of the Invention

[0009] The method for engraving and/or etching a material according to the present invention for achieving the foregoing object comprises the following steps (a) to (e):

(a) a process for exposing, to light, a layer of a water-soluble resin composition of a photo-sensitive laminate film which comprises a supporting sheet, an image mask-protection layer peelably adhered to the support-

ing sheet and a water-soluble resin composition layer having photocrosslinkability, wherein the water-soluble resin composition comprises a water-soluble polymer having photocrosslinkable groups in the polymer molecule, to thus cause crosslinking of the exposed areas of the resin layer to thereby form a predetermined pattern on the resin layer; (b) a process for dissolving out the non-crosslinked portion on the layer of the water-soluble photo-sensitive resin composition by developing the layer with water to thus form an image-carrying mask which is constituted from the crosslinked areas of the photo-sensitive resin composition remaining on the image mask-protection layer; (c) a process for adhering the photo-sensitive laminate film on which the images are formed to the surface of a material to be processed by contact-bonding; (d) a process for peeling off the supporting sheet from the photo-sensitive laminate film; and (e) a process for engraving and/or etching the material to be processed through the image-carrying mask adhered to the material, while the image mask-protection layer is removed. According to the foregoing processes, fine and precise images can be easily and precisely formed on a material to be processed through the photo-duplicating method. In addition, exposure and development processings are very simple since the photo-sensitive material is in the form of a film. Moreover, the development processing is safe and economical since it is performed with a developer simply comprising water. The surface of the image-carrying mask obtained after development exhibits strong adhesion and correspondingly the mask can be adhered to the material to be processed without using any adhesive. Further, the supporting sheet can easily be peeled off because of a presence of the image mask-protection layer after fine pictures and/or patterns are transferred to the material to thus prevent the aberration of the position of images and the removal of fine portions of the images can be prevented during sand blasting. Thus, the precise engraving and/or etching of a desired patterns and/or pictures can be performed.

[0010] The present invention also provides a photo-sensitive laminate for uses in making an image-carrying mask comprising a supporting sheet, an image mask-protection layer peelably adhered to the supporting sheet and a layer of a water-soluble resin composition having photocrosslinkability applied onto the image mask-protection layer, wherein the water-soluble resin composition comprises a water-soluble polymer having photocrosslinkable groups in the polymer molecule, to thus cause crosslinking of the exposed area of the resin layer to thereby form a predetermined pattern on the resin layer, and wherein the photocrosslinked resin layer of the image-carrying mask is capable of being contact-bonded to the surface of a material to be processed.

[0011] In the method of the present invention, the treatment with water in the process (b) is preferably performed by previously immersing the photo-sensitive laminate film which has been exposed to light through a

pattern to swell the non-crosslinked portion on the layer of the water-soluble resin composition and then washing with water. Thus, the non-crosslinked portion on the layer of the water-soluble resin composition can be completely removed and hence clear images can be obtained.

[0012] In the process (c), the photo-sensitive laminate film is preferably adhered to a material to be processed while applying a pressure or heating the same. Alternatively, the process (c) can be performed by applying, to the layer of the crosslinked water-soluble resin composition, an aqueous solution of sodium periodate, lithium chloride, lithium bromide, lithium nitrate, calcium chloride or ammonium thiocyanate to swell or solubilize the layer and then adhering the photo-sensitive laminate film to the material to be processed under pressure.

[0013] The process (e) for engraving or etching the material to be processed is preferably performed according to engraving or etching through sand blast. Likewise, the process (e) may be performed according to the engraving or etching with a chemical.

[0014] The photo-sensitive laminate film used in the method for engraving or etching a material to be processed comprises a supporting sheet, an image mask-protection layer peelably adhered to the supporting sheet and a layer of a water-soluble resin composition having photocrosslinkability. The water-soluble resin composition having photocrosslinkability may be a composition comprising a water-soluble polymer having a photocrosslinkable groups in the molecule selected from polyvinyl alcohol which is subjected to modification with acetal to introduce stilbazolium groups therein and polyvinyl alcohol to which N-methylolacrylamide is added. The layer of the water-soluble resin composition having photocrosslinkability preferably has a thickness ranging from 0.03 to 2mm. If the thickness of the layer is limited to the range defined above, the image-mask obtained after development of the layer exhibits sufficient resistance to the sand blasting or etching with a chemical during the process for engraving or etching the material to be processed. The image mask-protection layer of the photo-sensitive laminate film for making an image-carrying mask is preferably prepared from a member selected from the group consisting of polyvinyl alcohol, polyvinyl alcohol derivatives, polyvinyl butyral, ethyl cellulose, cellulose acetate and cellulose nitrate. Moreover, the image mask-protection layer is made from a material different from that for the supporting sheet and may be obtained from a member selected from the group consisting of polyvinyl chloride, polystyrene and polyamide. If the material for forming the image mask-protection layer is limited to these specific ones, the image mask-protection layer is weakly adhered to the supporting sheet during the development processing and can easily be peeled off therefrom, while it is relatively strongly adhered to the layer of the water-soluble resin composition, i. e., to the image-

carrying mask. The thickness of the image mask-protection layer preferably ranges from 1 to 30 μ m. This is because, if the thickness thereof falls within the range defined above, the image-carrying mask can be supported by the layer without causing any breakage and the mask can easily be removed during the process for engraving and/or etching the material to be processed without any difficulty.

Brief Description of Drawings

[0015]

Fig. 1 is a cross-sectional view of the photo-sensitive laminate film for image-masks according to the present invention; and Figs. 2 to 10 are diagrams for illustrating, in order, the method for engraving and/or etching with the aid of an image-carrying mask according to the present invention.

Description of Preferred Embodiments

[0016] The preferred embodiments of the present invention will hereunder be explained in more detail, but the present invention is not restricted to these specific embodiments at all.

[0017] Fig. 1 shows the construction of the photo-sensitive laminate film for an image-carrying mask used in the method for engraving and/or etching a material with the use of such an image-carrying mask according to the present invention. In the photo-sensitive laminate film 10 for an image-carrying mask, an image mask-protection layer 12 is adhered to a supporting sheet 11 obtained from a polyester film having a thickness of 75 μ m. The image mask-protection layer 12 comprises a layer of ethyl cellulose having a thickness of about 5 μ m formed according to a coating technique. A layer 13 of a water-soluble resin composition having photocrosslinkability having a thickness of 80 μ m is formed on the image mask-protection layer 12, the layer 13 being formed by coating a solution containing polyvinyl alcohol, an ethylene/vinyl acetate copolymer resin, a diazo resin, a water-dispersible pigment and a non-ionic surfactant, i.e., polyoxyethylene laurylphenyl ether and then drying the coated layer.

[0018] The method for engraving and/or etching a material with an image-carrying mask according to the present invention can be practiced with the aid of the photo-sensitive laminate film 10 for making an image-carrying mask in accordance with the processes as shown in the attached Figs. 2 to 10. As is shown in Fig. 2, an original positive film 15 carrying fine pictures and patterns comes in close contact with the surface of the water-soluble resin composition-layer 13 of the photo-sensitive laminate film 10 and is irradiated with light 16 from a metal halide lamp. Then, as shown in Fig. 3, the original positive film 15 is peeled off from the photo-sensitive laminate film 10. If the exposed photo-

sensitive laminate film 10 is immersed in water 17, the exposed portion thereof 13a is not swollen since it is crosslinked, but non-crosslinked unexposed portion 13b gets swollen and is soluble in water as shown in Fig. 4. As shown in Fig. 5, if water 19 is sprayed with a spraying device 18 to wash away the unexposed portion, only the exposed portion 13a remains as an image-carrying mask and the laminate film is thus developed. The resulting product is hot-air dried to give an image-carrying mask 13a on the image mask-protection layer 12 which is put on the supporting sheet 11.

[0019] As is shown in Fig. 6, the image-carrying mask 13a which is still supported by the supporting sheet 11 and the image mask-protection layer 12 is adhered and contact-bonded to a glass plate 20 while heating with an iron 21. Then, as shown in Fig. 7, the supporting sheet 11 is peeled off from the image mask-protection layer 12. Further, as shown in Fig. 8, the glass plate is engraved or etched by blasting abrasive particles 23 through the image mask-protection layer 12 using a sand blasting machine 22. Thus, the portion of the glass plate 20 to which the image-carrying mask 13a is adhered is not engraved and/or etched, while on the portion of the glass plate to which the image-carrying mask 13a is not adhered or which is covered with only the image mask-protection layer 12 is engraved and/or etched, the image mask-protection layer 12 is completely removed and the surface of the glass plate 20 is engraved and etched as shown in Fig. 9. After the completion of the sand blasting operation, the remaining abrasive 23 and the image-carrying mask 13a are washed out so that the glass plate 20 on which the image is engraved or etched is completed as shown in Fig. 10.

[0020] The following variations can be made to the foregoing embodiment.

[0021] As the supporting sheet 11, there may be used, for instance, a polypropylene film, a polyethylene film, a polystyrene film, a polyvinyl chloride film, a polycarbonate film, synthetic paper or paper coated with a synthetic resin in addition to the polyester film used in the embodiment. Moreover, the thickness of the supporting sheet 11 may be adjusted within the range of from 50 to 500 μm .

[0022] In the foregoing embodiment, the layer 13 of the water-soluble resin composition used has a thickness of 80 μm . However, the thickness thereof may be varied between 0.03 to 2 mm and it is thus preferred to properly control the thickness thereof depending on the depth to be engraved and/or etched so that the image-carrying mask obtained after development shows proper resistance to sand blasting or chemicals. If the depth to be engraved is great, the thickness thereof should be adjusted within the range of from 0.1 to 2mm so as to withstand the processing over a long time period, while if the depth to be engraved is small, it is sufficient to adjust the thickness to 30 to 80 μm .

[0023] In the foregoing embodiment, the exposure

process shown in Fig. 2 is performed by irradiating with the light 16 from a metal halide lamp, but it is also possible to use other light sources which emit actinic rays having a wave length ranging from 300 to 500 nm such as an arc lamp, a xenon lamp or a high pressure mercury lamp.

[0024] The development processing as shown in Fig. 5 is carried out by spraying water 19 using a spraying machine 18, but it is also effective to lightly rub the surface with a brush or a sponge simultaneously with such a spraying operation to wash out the non-exposed portion and to thus develop the laminate film.

[0025] In the process shown in Fig. 8, the engraving or etching process is performed by blasting the abrasive particles 23 with the aid of the sandblasting machine 22, but the etching with a chemical is likewise effective. Examples of chemicals used in the engraving or etching treatment are an aqueous solution of hydrofluoric acid when the materials to be processed are glass and stones, an aqueous solution of ferric chloride when the materials are copper and copper alloys, and aqueous solutions of hydrochloric acid and sulfuric acid when they are other metals.

[0026] The present invention will hereunder be explained in more detail with reference to the following specific example.

Example 1.

[0027] There was dissolved, in water, a stilbazolium-added polyvinyl alcohol which was prepared by subjecting, to a reaction with acetal, polyvinyl alcohol having an average degree of polymerization of 1,700 and degree of saponification of 88 mole % (available from Shin Etsu Chemical Co., Ltd. under the trade name of PA-18) to add 1.4 mole % of N-methyl- γ -(p-formylstyryl)-pyridinium methosulfate to thus give a solution having a concentration of 15% by weight. 15 parts by weight of an acrylate oligomer (available from Toagosei Chemical Industry Ltd. under the trade name of Aronix M-8030), 15 parts by weight of pentaerythritol triacrylate and 3 parts by weight of 2-chlorothioxanthone (available from Nippon Kayaku Co., Ltd. under the trade name of Kayacure CTX) were added to and dispersed in the foregoing solution. 55 parts by weight of a 50% by weight polyvinyl acetate emulsion and 0.2 part by weight of a water-dispersible purple pigment were added to and mixed with the resulting dispersion to thus prepare a mixed solution of a photo-sensitive resin composition. This mixed solution of the photo-sensitive resin composition was applied onto the surface of an image mask-protection layer applied to a supporting sheet similar to those used in Example 1 of EP-A-0 506 959 and then dried to give a photo-sensitive laminate film carrying a layer of the photo-sensitive resin composition having a thickness of 100 μm .

[0028] The same procedures used in Example 1 of EP-A-0 506 959 were repeated to give an image-carry-

ing mask using the photo-sensitive laminate film. There was not observed any separation between the supporting sheet and the image mask-protection layer and between the image mask-protection layer and the layer of the photo-sensitive resin composition, i.e., the image-carrying mask during the development processing.

[0029] The image-carrying mask thus obtained which had been still carried by the supporting sheet and the image mask-protection layer was adhered to a glass plate having a thickness of 8 mm on which a 1% aqueous solution of sodium periodate was coated and subjected to contact bonding. Then the supporting sheet was peeled off from the image mask-protection layer. The supporting sheet was easily be separated from the image mask-protection layer, but the adhesion between the image mask-protection layer and the image-carrying mask was strong and, therefore, there was not observed any aberration of the relative position between the image-carrying mask and the glass plate.

[0030] A 50% by weight aqueous solution of hydrofluoric acid was applied onto the surface of the resulting assembly which comprised the glass plate, the image-carrying mask adhered to the glass plate and the image mask-protection layer on the image-carrying mask, on the side of the image mask-protection layer. After about 2 minutes, the assembly was sufficiently washed with water to wash out the aqueous hydrofluoric acid solution as well as the remaining image-carrying mask. The portion of the glass plate to which the image-carrying mask had been adhered was not corroded with the hydrofluoric acid aqueous solution. On the other hand, the image mask-protection layer was approximately easily be removed and the portion of the glass plate to which any image-carrying mask had not been adhered, i.e., that covered with only the image mask-protection layer was corroded and dissolved out to a depth of about 50 μ m. Thus, the fine picture and patterns of the original were faithfully etched on the glass plate.

Industrial Applicability

[0031] According to the method for engraving and/or etching according to the present invention, fine and precise images can be engraved and/or etched on the surface of a material to be processed such as glass, metals and plastics. The photo-sensitive laminate film for making an image-carrying mask used in the engraving and/or etching method can be handled in the form of a film during preparing the image-carrying mask and thus the handling thereof during the exposure to light and the development is very simple. In addition, since the development thereof can be performed with a developer simply comprising water, the film is safe and economical. The image-carrying mask obtained after development can be adhered to a material to be processed without using any adhesive since the surface thereof has adherence and does not cause the aberration

tion of the position relative to the material to be processed even if it carries fine pictures and patterns because of a presence of the image mask-protection layer. Moreover, the image mask-protection layer serves to prevent the separation of fine portions of the image during the sand blasting operation and as a result, precise engraving can be performed.

Claims

1. A method for engraving and/or etching a material comprising the following steps (a) to (e):

- (a) a process for exposing, to light (16), a water-soluble resin composition layer of a photo-sensitive laminate film (10) which comprises a supporting sheet (11), an image mask-protection layer (12) peelably adhered to the supporting sheet and a layer of a water-soluble resin composition having photocrosslinkability (13), wherein the water-soluble resin composition comprises a water-soluble polymer having photocrosslinkable groups in the polymer molecule, to thus cause crosslinking of the exposed area of the resin layer to thereby form a predetermined pattern on the resin layer;
- (b) a process for dissolving out the non-crosslinked portion (13b) on the layer of the water-soluble photo-sensitive resin composition by developing the layer with water (17, 19) to thus form an image-carrying mask (13a) which is constituted from the crosslinked area of the photo-sensitive resin composition remaining on the image mask-protection layer;
- (c) a process for adhering the photo-sensitive laminate film on which the images are formed to the surface of a material (20) to be processed by contact-bonding;
- (d) a process for peeling off the supporting sheet (11) from the photo-sensitive laminate film, and
- (e) a process for engraving and/or etching the material (20) to be processed through the image-carrying mask adhered to the material, while the image mask-protection layer is removed.

2. The method of claim 1 wherein the treatment with water in the process (b) is performed by previously immersing the photo-sensitive laminate film to swell the layer of the water-soluble resin composition and then washing with water.

3. The method of claim 1 wherein the process (c), the photo-sensitive laminate film is adhered to a material to be processed while applying a pressure to the film and heating the same.

4. The method of claim 1 wherein the process (c) is performed by applying, to the layer of the water-soluble resin composition, an aqueous solution of at least one member selected from the group consisting of sodium periodate, lithium chloride, lithium bromide, lithium nitrate, calcium chloride and ammonium thiocyanate to swell or solubilize the crosslinked water-soluble resin composition and then adhering the photo-sensitive laminate film to the material to be processed under pressure. 5
5. The method of claim 1 wherein the process (e) is an engraving treatment by sand blasting. 10
6. The method of claim 1 wherein the process (e) is an engraving treatment with a chemical. 15
7. The method of claim 1, wherein the water-soluble polymer having photocrosslinkable groups in the polymer molecule, as comprised in the water-soluble resin composition in process step (a), is a polyvinyl alcohol which had been subjected to modification with acetal to introduce stilbazolium groups therein. 20
8. A photo-sensitive laminate film (10) for uses in making an image-carrying mask comprising a supporting sheet (11), an image mask-protection layer (12) peelably adhered to the supporting sheet and a layer of a water-soluble resin composition having photocrosslinkability (13) applied onto the image mask-protection layer (12), wherein the water-soluble resin composition comprises a water-soluble polymer having photocrosslinkable groups in the polymer molecule, to thus cause crosslinking of the exposed area of the resin layer to thereby form a predetermined pattern on the resin layer, and wherein the photocrosslinked resin layer of the image-carrying mask is capable of being contact-bonded to the surface of a material to be processed. 25 30 35 40
9. The photo-sensitive laminate film for use in making an image-carrying mask of claim 8 wherein the water-soluble resin composition having photocrosslinkability comprises a water-soluble polymer having a photo-crosslinkable group in the molecule selected from polyvinyl alcohol which is subjected to modification with acetal to introduce stilbazolium groups therein and polyvinyl alcohol to which N-methylolacrylamide is added. 45 50
10. The photo-sensitive laminate film for use in making an image-carrying mask of claim 8 wherein the layer of the water-soluble resin composition having photocrosslinkability has a thickness ranging from 0.04 to 2 mm. 55

11. the photo-sensitive laminate film for use in making an image-carrying mask of claim 8 wherein the image mask-protection layer is prepared from a member selected from the group consisting of polyvinyl alcohol, polyvinyl alcohol derivatives, polyvinyl butyral, ethyl cellulose, cellulose acetate and cellulose nitrate and the thickness of the image mask-protection layer ranges from 1 to 30 μm .
12. The photo-sensitive laminate film for use in making an image-carrying mask of claim 8 wherein the image mask-protection layer is prepared from a material different from that for the supporting sheet and is obtained from a member selected from the group consisting of polyvinyl chloride, polystyrene and polyamide and the thickness of the image mask-protection layer ranges from 1 to 30 μm .

Patentansprüche

1. Verfahren zur Gravierung und/oder Ätzung eines Materials, welches die folgenden Schritte (a) bis (e) umfasst:
 - (a) einen Verfahrensschritt zur Belichtung mit Licht (16) einer Schicht einer wasserlöslichen Harzzusammensetzung eines lichtempfindlichen Laminatfilms (10), der eine Trägerlage (11), eine auf der Trägerlage abziehbar angeheftete Bildmaskenschutzschicht (12) und eine Schicht einer wasserlöslichen Harzzusammensetzung mit Lichtvernetzbarkeit (13) umfasst, wobei die wasserlösliche Harzzusammensetzung ein wasserlösliches Polymer mit lichtvernetzenden Gruppen in dem Polymermolekül umfasst, um so eine Vernetzung des belichteten Bereichs der Harzschicht zu bewirken, um dadurch ein vorbestimmtes Muster auf der Harzschicht zu bilden;
 - (b) einen Verfahrensschritt zur Herauslösung der nicht-vernetzten Teile (13b) auf der Schicht der wasserlöslichen, lichtempfindlichen Harzzusammensetzung durch das Entwickeln der Schicht mit Wasser (17, 19), um so eine bildtragende Maske (13a) zu bilden, die aus den vernetzten Bereichen der lichtempfindlichen Harzzusammensetzung, die auf der Bildmaskenschutzschicht zurückgeblieben sind, aufgebaut ist;
 - (c) einen Verfahrensschritt zur Anheftung des lichtempfindlichen Laminatfilms, auf dem die Abbilder gebildet sind, auf die Oberfläche eines zu verarbeitenden Materials (20) durch Kontaktbinden;
 - (d) einen Verfahrensschritt zur Ablösung der

Trägerlage (11) von dem lichtempfindlichen Laminatfilm, und

(e) einen Verfahrensschritt zur Gravierung und/oder Ätzung des zu verarbeitenden Materials (20) durch die auf dem Material angeheftete bildtragende Maske hindurch, während die Bildmaskenschutzschicht entfernt wird.

2. Verfahren nach Anspruch 1, wobei die Behandlung mit Wasser in dem Verfahrensschritt (b) durch vorheriges Eintauchen des lichtempfindlichen Laminatfilms, um die Schicht der wasserlöslichen Harzzusammensetzung aufzuquellen, und nachfolgendem Waschen mit Wasser durchgeführt wird.
3. Verfahren nach Anspruch 1, wobei in dem Verfahrensschritt (c) der lichtempfindliche Laminatfilm auf das zu verarbeitende Material angeheftet wird, während Druck auf den Film ausgeübt wird und derselbe beheizt wird.
4. Verfahren nach Anspruch 1, wobei der Verfahrensschritt (c) durchgeführt wird mittels:

Auftragung einer wässrigen Lösung wenigstens eines Elements, das aus der aus Natriumperiodat, Lithiumchlorid, Lithiumbromid, Lithiumnitrat, Calciumchlorid und Ammoniumthiocyanat bestehenden Gruppe ausgewählt ist, auf die Schicht der wasserlöslichen Harzzusammensetzung, um die vernetzte wasserlösliche Harzzusammensetzung aufzuquellen oder zu lösen, und danach Anheftung des lichtempfindlichen Laminatfilms auf das zu verarbeitende Material unter Druck.

5. Verfahren nach Anspruch 1, wobei der Verfahrensschritt (e) eine Gravierbehandlung durch Sandstrahlen ist.
6. Verfahren nach Anspruch 1, wobei der Verfahrensschritt (e) eine Gravierbehandlung mit einer Chemikalie ist.
7. Verfahren nach Anspruch 1, wobei das wasserlösliche Polymer mit lichtvernetzbaaren Gruppen in dem Polymermolekül, wie es in der wasserlöslichen Harzzusammensetzung im Verfahrensschritt (a) umfasst ist, ein Polyvinylalkohol ist, der einer Modifizierung mit Acetal unterworfen worden ist, um darin Stilbazoliumgruppen einzuführen.
8. Lichtempfindlicher Laminatfilm (10) für die Verwendung zur Herstellung einer bildtragenden Maske, die eine Trägerlage (11), eine auf der Trägerlage abziehbar angeheftete Bildmaskenschutzschicht (12) und eine Schicht einer wasserlöslichen Harz-

zusammensetzung mit Lichtvernetzbarkeit (13), die auf der Bildmaskenschutzschicht (12) aufgetragen ist, umfasst, wobei die wasserlösliche Harzzusammensetzung ein wasserlösliches Polymer mit lichtvernetzbaaren Gruppen in dem Polymermolekül umfasst, um so eine Vernetzung des belichteten Bereichs der Harzschicht zu bewirken, um dadurch ein vorbestimmtes Muster auf der Harzschicht zu bilden, und wobei die lichtvernetzte Harzschicht der bildtragenden Maske zur Kontaktbindung auf die Oberfläche eines zu verarbeitenden Materials fähig ist.

9. Lichtempfindlicher Laminatfilm für die Verwendung zur Herstellung einer bildtragenden Maske nach Anspruch 8, wobei die wasserlösliche Harzzusammensetzung mit Lichtvernetzbarkeit ein wasserlösliches Polymer mit lichtvernetzbaaren Gruppen in dem Molekül umfasst, welches aus Polyvinylalkohol der einer Modifizierung mit Acetal unterworfen worden ist, um Stilbazoliumgruppen darin einzuführen, und Polyvinylalkohol, zu dem N-Methylolacrylamid zugegeben ist, ausgewählt ist.
10. Lichtempfindlicher Laminatfilm für die Verwendung zur Herstellung einer bildtragenden Maske nach Anspruch 8, wobei die Schicht der wasserlöslichen Harzzusammensetzung mit Lichtvernetzbarkeit eine im Bereich von 0,04 bis 2 mm liegende Dicke aufweist.
11. Lichtempfindlicher Laminatfilm für die Verwendung zur Herstellung einer bildtragenden Maske nach Anspruch 8, wobei die Bildmaskenschutzschicht aus einem Element hergestellt ist, das aus der aus Polyvinylalkohol, Polyvinylalkoholderivaten, Polyvinylbutyral, Ethylcellulose, Celluloseacetat und Cellulosenitrat bestehenden Gruppe ausgewählt ist, und wobei die Dicke der Bildmaskenschutzschicht in einem Bereich von 1 bis 30 µm liegt.
12. Lichtempfindlicher Laminatfilm für die Verwendung zur Herstellung einer bildtragenden Maske nach Anspruch 8, wobei die Bildmaskenschutzschicht aus einem Material hergestellt ist, das unterschiedlich zu dem der Trägerlage ist, und aus einem Element erhalten wird, das aus der aus Polyvinylchlorid, Polystyrol und Polyamid bestehenden Gruppe ausgewählt ist, und wobei die Dicke der Bildmaskenschutzschicht in einem Bereich von 1 bis 30 µm liegt.

Revendications

1. Procédé de gravure mécanique et/ou chimique d'un matériau, comprenant les étapes (a) à (e) ci-après :
(a) une étape pour exposer à la lumière (16)

une couche d'une composition de résine soluble dans l'eau d'un film stratifié photosensible (10) qui comprend une feuille support (11), une couche protectrice de masque image (12), qui adhère d'une manière pelable à la feuille support, et une couche d'une composition de résine photoréticulable soluble dans l'eau (13), où la composition de résine soluble dans l'eau comprend un polymère soluble dans l'eau comportant des groupes photoréticulables dans la molécule du polymère, pour provoquer de ce fait une réticulation de la zone exposée de la couche de résine, dans le but de former une configuration prédéterminée sur la couche de résine ;

(b) une étape pour éliminer par dissolution la portion non-réticulée (13b) se trouvant sur la couche de la composition de résine photosensible soluble dans l'eau, par développement de la couche avec de l'eau (17, 19), pour former de ce fait un masque portant image (13a), qui est constitué de la zone réticulée de la composition de résine photosensible restant sur la couche de protection du masque image ;

(c) une étape pour faire adhérer à la surface d'un matériau (20) devant être traité par collage par contact le film stratifié photosensible sur lequel sont formées les images ;

(d) une étape pour enlever par pelage la feuille support (11) du film stratifié photosensible ; et

(e) une étape pour graver par voie mécanique et/ou chimique le matériau (20) devant être traité, à travers le masque portant image qui adhère au matériau, tandis que la couche de protection du masque image est enlevée.

2. Procédé selon la revendication 1, dans lequel le traitement à l'eau dans l'étape (b) est mis en oeuvre par immersion préalable du film stratifié photosensible pour provoquer le gonflement de la couche de la composition de résine soluble dans l'eau, puis lavage à l'eau.
3. Procédé selon la revendication 1, dans lequel, dans l'étape (c), le film stratifié photosensible est mis à adhérer à un matériau devant être traité, tout en appliquant une pression au film et en chauffant ce dernier.
4. Procédé selon la revendication 1, dans lequel l'étape (c) est mise en oeuvre par application, à la couche de la composition de résine soluble dans l'eau, d'une solution aqueuse d'au moins un composé choisi dans l'ensemble comprenant le pero-

date de sodium, le chlorure de lithium, le bromure de lithium, le nitrate de lithium, le chlorure de calcium et le thiocyanate d'ammonium, pour faire gonfler ou solubiliser la composition de résine réticulée soluble dans l'eau, ce après quoi on colle sous pression le film stratifié photosensible au matériau devant être traité.

5. Procédé selon la revendication 1, dans lequel l'étape (e) est un traitement de gravure mécanique par sablage.
6. Procédé selon la revendication 1, dans lequel l'étape (e) est un traitement de gravure utilisant un produit chimique.
7. Procédé selon la revendication 1, dans lequel le polymère soluble dans l'eau comportant des groupes photoréticulables dans la molécule du polymère, en tant qu'il est compris dans la composition de résine soluble dans l'eau de l'étape (a), est un poly(alcool vinylique) qui a été soumis à une modification par un acétal pour y introduire des groupes stilbazolium.
8. Film stratifié photosensible (10), pour utilisations lors de la fabrication d'un masque portant image, comprenant une feuille support (11), une couche (12) de protection du masque image, qui adhère d'une manière pelable à la feuille support, et une couche d'une composition de résine réticulable soluble dans l'eau (13), appliquée sur la couche de protection du masque image (12), où la composition de résine soluble dans l'eau comprend un polymère soluble dans l'eau comportant des groupes photoréticulables dans la molécule du polymère, pour provoquer de ce fait une réticulation de la zone exposée de la couche de résine, et ainsi former une configuration prédéterminée sur la couche de résine, et où la couche de résine photoréticulée du masque portant image est à même d'être collée par contact à la surface du matériau à traiter.
9. Film stratifié photosensible, pour utilisation dans la fabrication d'un masque portant image selon la revendication 8, dans lequel la composition de résine réticulable soluble dans l'eau comprend un polymère soluble dans l'eau ayant un groupe photoréticulable dans sa molécule, choisi parmi un poly(alcool vinylique) qui est soumis à une modification par un acétal pour y introduire des groupes stilbazolium et un poly(alcool vinylique) auquel est ajouté un N-méthylolacrylamide.
10. Film stratifié photosensible, pour utilisation dans la fabrication d'un masque portant image selon la revendication 8, dans lequel la couche de la composition de résine réticulable soluble dans l'eau a

une épaisseur de 0,04 à 2 mm.

11. Film stratifié photosensible, pour utilisation dans la fabrication d'un masque portant image selon la revendication 8, dans lequel la couche de protection du masque image est préparée à partir d'un composé choisi dans l'ensemble comprenant le poly(alcool vinylique), les dérivés du poly(alcool vinylique), le polyvinylbutyral, l'éthylcellulose, l'acétate de cellulose et le nitrate de cellulose, et l'épaisseur de la couche de protection du masque image est comprise entre 1 et 30 μm .
12. Film stratifié photosensible, pour utilisation dans la fabrication d'un masque portant image selon la revendication 8, dans lequel la couche de protection du masque image est préparée à partir d'un matériau différent de celui de la feuille support et est obtenue à partir d'un composé choisi dans l'ensemble comprenant le poly(chlorure de vinyle), le polystyrène et le polyamide, et l'épaisseur de la couche de protection du masque image est comprise entre 1 et 30 μm .

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FIG. 1

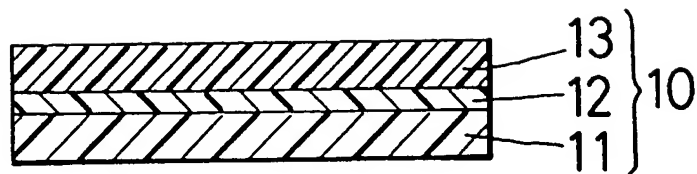


FIG. 2

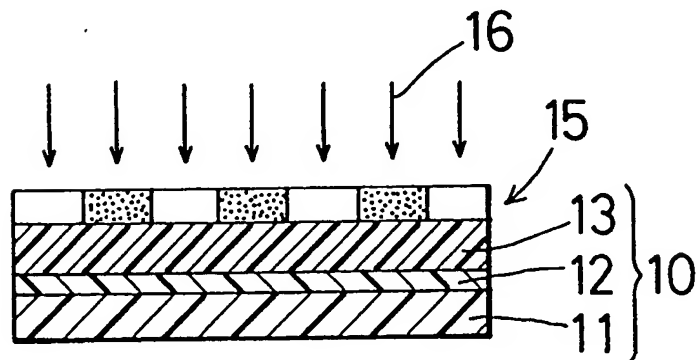


FIG. 3

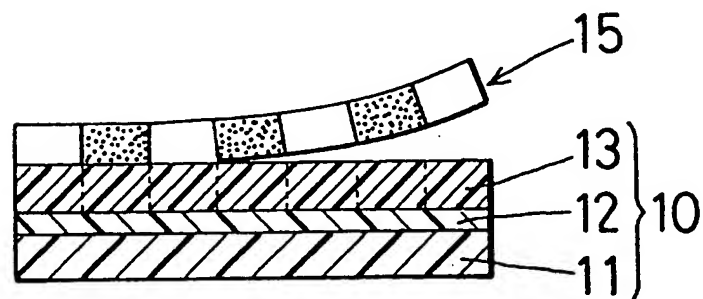


FIG. 4

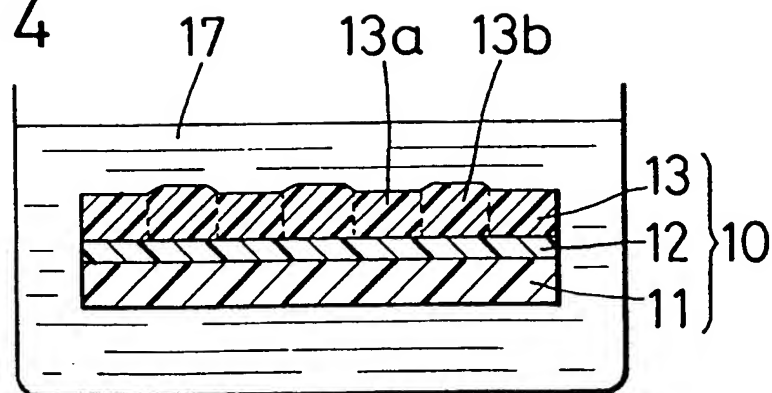


FIG. 5

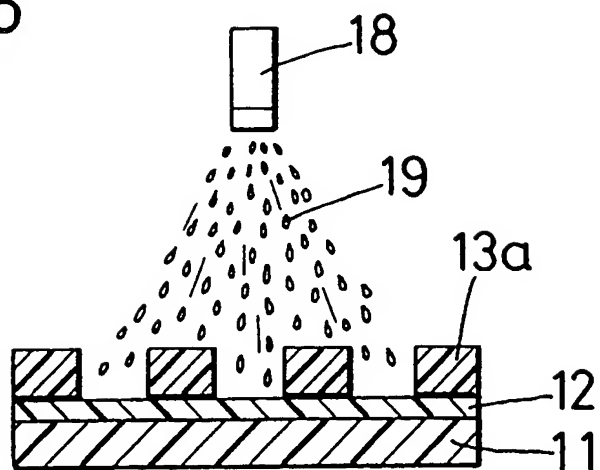


FIG. 6

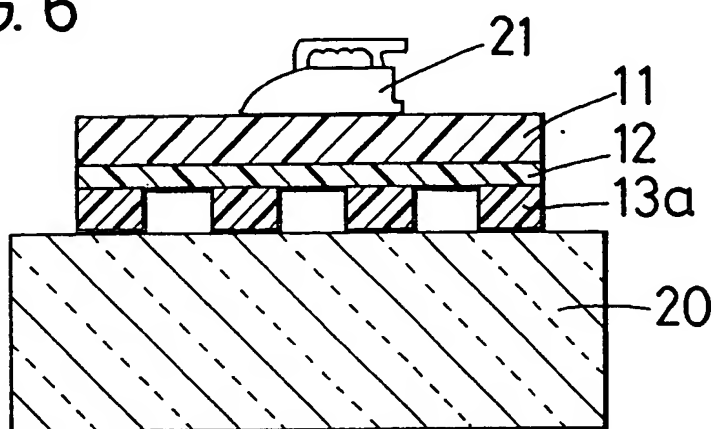


FIG. 7

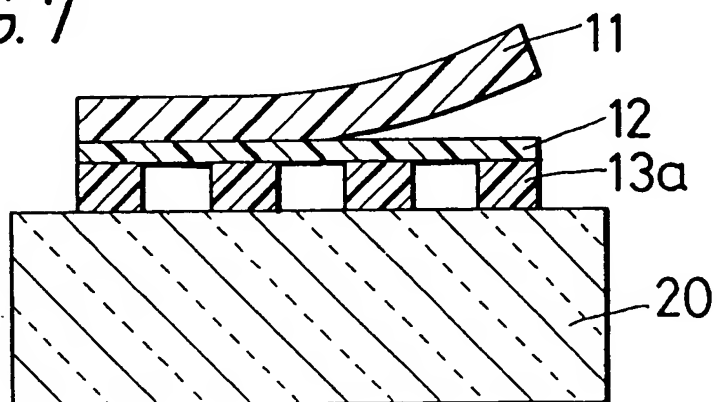


FIG. 8

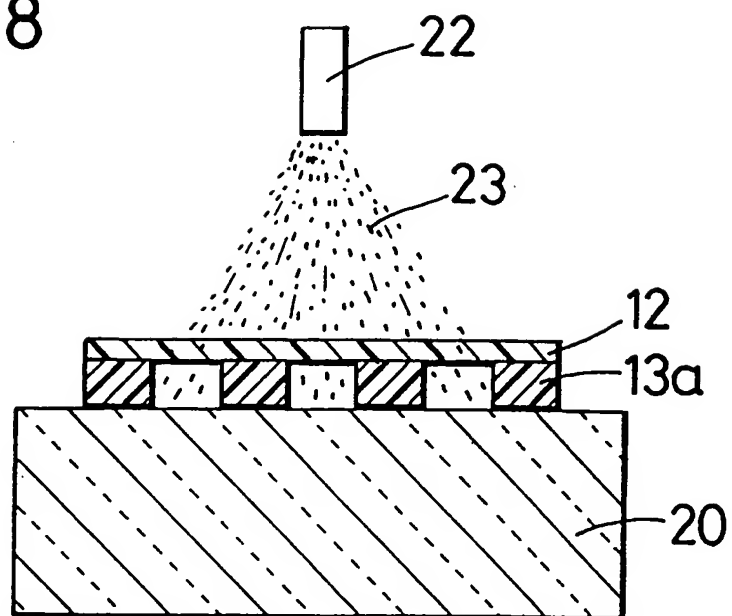


FIG. 9

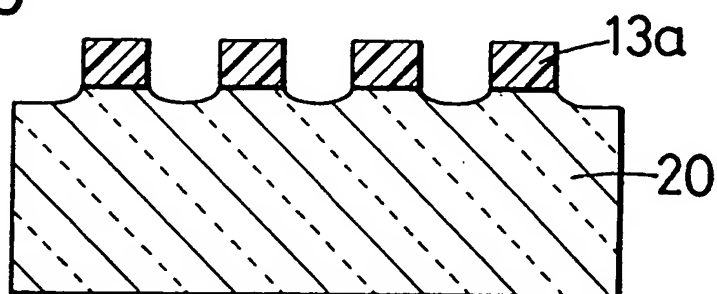


FIG. 10

